National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2717a

Sulfur in Residual Fuel Oil (3 %)

This Standard Reference Material (SRM) is intended for use in the calibration of instruments and the evaluation of methods used in the determination of total sulfur in fuel oils or materials of similar matrix. A unit of SRM 2717a consists of 100 mL of commercial "No. 6" residual fuel oil as defined by ASTM D396-97 Specification for Fuel Oils [1].

Certified Value: The certified sulfur content reported in Table 1 is based on analyses by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [2]. Homogeneity testing was performed using X-ray fluorescence (XRF) spectrometry. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST. The uncertainty in the certified value is expressed as an expanded uncertainty and is calculated according to the method in the ISO and NIST Guides [3]. The expanded uncertainty is based on a 95 % confidence interval.

Table 1. Certified Value

Sulfur (mass fraction):	2.9957 % ± 0.0032 %

Information Values: The information values reported in Table 2 are noncertified values with no uncertainty assessed. They are provided as supplemental information to better characterize the matrix.

ASTM Information: SRM 2717a was included as an unknown in the January 1997 ASTM Committee D-2 Interlaboratory Crosscheck Program for No. 6 Fuel Oil as Sample ID: #6F9701. Summary statistics reported by ASTM are provided in the addendum to this certificate to demonstrate user experience with this material using ASTM methods and to better characterize the matrix. The ASTM Committee D-2 Interlaboratory Crosscheck results were not used in calculating the certified sulfur value for SRM 2717a and should not be used as a substitute for the NIST certified value.

Expiration of Certification: The certification of this SRM is valid until **01 October 2010**, within the uncertainty specified, provided the SRM is handled and stored in accordance with the instructions given in the certificate (see "Instructions for Use"). However, the certification will be nullified if the SRM is damaged, contaminated, or otherwise modified.

Stability: This material is considered to be stable during the period of certification. NIST will monitor this material and will report any significant changes in certification to the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of the technical measurements leading to certification of this SRM were performed by J.D. Fassett of the NIST Analytical Chemistry Division.

Analytical measurements were performed by W.R. Kelly, R.D. Vocke, A.F. Marlow, J.R. Sieber, and J.L. Mann of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 16 May 2006
See Certificate Revision History on Last Page

Robert L. Watters, Jr., Chief
Measurement Services Division

Statistical consultation for this SRM was provided by K.R. Eberhardt of the NIST Statistical Engineering Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

INSTRUCTIONS FOR USE

Because of the viscosity of SRM 2717a, it is recommended that the SRM unit be warmed slowly to between 40 °C and 60 °C and then shaken, or stirred with a clean stirrer, before sampling. Care must be exercised to not introduce entrapped air which could affect gravimetric measurements and XRF responses. A detailed study to determine if the sulfur components of SRM 2717a will segregate has not been performed.

The SRM bottle should only be opened for the minimum time required to dispense the material. To relate analytical determinations to the certified value in this Certificate of Analysis, a minimum sample mass of 140 mg should be used. After use, the bottle should be tightly recapped and stored under normal laboratory conditions away from direct sunlight.

SUPPLEMENTAL INFORMATON

Information Values: The information values given in Table 2 are based on results provided by either a commercial or industrial laboratory using ASTM methods. They are given as additional information on the matrix only.

Table 2. Information Values

Measurement		ASTM Standard Used [4,5]	Result
Kinematic Viscosity @	40 °C	D445-94	540.2 × 10^{-6} m^2/s (540.2 cSt)
@	50 °C	D445-94	282.0 × 10^{-6} m^2/s (282.0 cSt)
@	100 °C	D445-94	31.7 × 10^{-6} m^2/s (31.7 cSt)
Carbon		D5291-92	85.9 %
Hydrogen		D5291-92	10.3 %

REFERENCES

[1] ASTM D396-97, *Standard Specification for Fuel Oils*; Annu. Book ASTM Stand. Vol. 05.01, West Conshohocken, PA.

[2] Kelly, W.R.; Paulsen, P.J.; Murphy, K.E.; Vocke, R.D., Jr.; Chen, L.-T.; *Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry*; Anal. Chem., Vol. 66, pp. 2505–2513 (1994).

[3] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, lst ed. International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

[4] ASTM D445-94, *Test Method of Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)*; Annu. Book ASTM Stand., Vol. 10.03, West Conshohocken, PA.

[5] ASTM D5291-96, *Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants*; Annu. Book ASTM Stand., Vol. 05.03, West Conshohocken, PA.

Certificate Revision History: 16 May 2006 (Editorial changes); 01 March 2006 (Editorial changes); 05 January 2000 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Telephone (301) 975-6776 Fax (301) 926-4751, e-mail srminfo@nist.gov, or via the Internet at http://www.nist.gov/srm.

Addendum

Standard Reference Material® 2717a

Sulfur in Residual Fuel Oil (3 %)

ASTM Committee D-2 Interlaboratory Crosscheck Program Results: SRM 2717a was included as an unknown in the January 1997 ASTM Committee D-2 Interlaboratory Crosscheck Program for No. 6 Fuel Oil as Sample ID: #6F9701. Summary statistics reported by ASTM are provided in the addendum to this certificate to demonstrate user experience with this material using ASTM methods and to better characterize the matrix. The ASTM Committee D-2 Interlaboratory Crosscheck results were not used in calculating the certified sulfur value for SRM 2717a and should not be used as a substitute for the NIST certified value.

Gaithersburg, MD 20899
Addendum Issue Date: 16 May 2006

Robert L. Watters, Jr., Chief
Measurement Services Division

Summary Statistics Reported in the May 1998 ASTM Committee D-2 Interlaboratory Crosscheck Program for No. 6 Fuel Oil

Analyte	No. Valid Results	Robust[a] Mean	Robust[a] Standard Deviation	Reproducibility ASTM Standard	Reproducibility These Test Data	Comments
Aluminum D 5184 (mg/kg) Method A: ICP	14	8.0	2.4	2.7	6.6	
Aluminum D 5184 (mg/kg) Method B: AAS	29	7.1	2.0	2.4	5.5	
Silicon D 5184 (mg/kg) Method A: ICP	14	10.6	3.0	5.6	8.3	
Silicon D 5184 (mg/kg) Method B: AAS	27	14.8	9.4	8.1	26.0	
API Gravity D 287 (°API)	72	11.22	0.31	0.50	0.86	
Ash D 482 (mass %)	84	0.0610	0.0082	0.0050	0.0227	
Asphaltenes D 3279 (NHI, %)	56	10.538	1.021	2.780	2.828	
Carbon Residue (Conradson) D 189 (mass %)	44	17.026	1.192	2.599	3.302	
Carbon Residue (Micro Method) D 4530 (mass %)	43	17.399	0.511	1.647	1.415	
Density D 1298 (kg/L) at 15 °C	62	0.99118	0.00142	0.00120	0.00393	Thirteen labs reported that their test results were initially developed in °F. This data is not included in the statistical analysis in that 15 °C is different enough from 60 °F to affect density.
Flash Point of Ordinary Liquids D 93 (°C) Manual/Automatic Procedure A (Corrected Flash Point)	94	73.12	4.91	5.70	13.60	Twenty-four labs reported that their test results were initially developed in °F. Four labs data were converted to °C.
Heat Content (Gross) D 240 (MJ/kg)	38	42.2924	0.3471	0.4000	0.9615	
Nitrogen D 3228 (mass %)	18	0.3991	0.0359	0.1200	0.0994	

Analyte	No. Valid Results	Robust[a] Mean	Robust[a] Standard Deviation	Reproducibility ASTM Standard	Reproducibility These Test Data	Comments
Nitrogen D 4629 (mg/kg)	20	3244.642	1143.172	See Comments	3166.586	One lab did not provide data in correct reporting units. Data not included in statistical analysis. ASTM D 4629 is applicable for the determination of nitrogen in the range of 0.3 mg/kg to 100 mg/kg. Results are above this range, therefore, ASTM Reproducibility not determined.
Nitrogen D 5291 (mass %)	6	0.4050	0.0537	See Comments	0.1487	ASTM D 5291 is not applicable to light materials or those containing < 0.75 mass % nitrogen. The ASTM precision statement addresses the concentration range of nitrogen from 0.75 mass % to 2.5 mass %. The Robust Mean is below this range, therefore ASTM Reproducibility not determined.
Nitrogen D 5762 (μg/g)	4	3823.750	609.772	1108.888	1689.068	
Pour Point D 97 Procedure A (°C) Manual/Automatic	74	-11.6	4.3	6.0	11.9	ASTM D 97 states to report pour point limits at temperatures in multiples of 3 °C. Test data from labs not reporting in multiples of 3 °C or results initially developed in °F are not included in the statistical analysis. Nine labs reported their test results were initially developed in °F. Six labs reported test results that were not multiples of three.
Sediment D 473 (mass %)	67	0.025	0.017	0.039	0.047	
Sediment D 4870 (m/m)	24	0.027	0.013	0.056	0.036	
Sulfur D 129 (mass %)	8	2.9415	0.1496	0.2700	0.4144	
Sulfur D 1552 (mass %) Iodate Procedure	3	2.9793	0.2061	0.2600	0.5709	
Sulfur D 2622 (mass %)	13	2.93206	0.07905	0.46913	0.21897	

Analyte	No. Valid Results	Robust[a] Mean	Robust[a] Standard Deviation	Reproducibility ASTM Standard	Reproducibility These Test Data	Comments
Sulfur D 4294 (mass %)	75	2.9342	0.0848	0.2227	0.2349	
Sulfur D 5453 (µg/g)						Statistical analysis of data not determined due to insufficient number of data points.
Vanadium D 1548 (mg/kg)	13	207.509	13.568	20.751	37.583	
Vanadium D 5708 (mg/kg) Method A: ICP with an Organic Solvent Specimen Solution	16	215.7514	23.2070	35.8466	64.2834	
Nickel D 5708 (mg/kg) Method A: ICP with an Organic Solvent Specimen Solution	15	51.2554	6.4575	10.7540	17.8873	
Iron D 5708 (mg/kg) Method A: ICP with an Organic Solvent Specimen Solution	15	21.7387	6.1760	See Comments	17.1075	The ASTM precision statement addresses the concentration range of iron from 1 mg/kg to 10 mg/kg. The Robust Mean is above this range, therefore ASTM Reproducibility not determined.
Vanadium D 5708 (mg/kg) Method B: ICP after Acid Decomposition	3	248.7667	30.4648	34.3061	84.3875	
Nickel D 5708 (mg/kg) Method B: ICP after Acid Decomposition	3	51.2667	1.2642	3.3997	3.5018	
Iron D 5708 (mg/kg) Method B: ICP after Acid Decomposition	3	28.1667	5.7344	See Comments	15.8843	The ASTM precision statement addresses the concentration range of iron from 1 mg/kg to 10 mg/kg. The Robust Mean is above this range, therefore ASTM Reproducibility not determined.
Vanadium D 5863 (mg/kg) Method A: AAS (Decomposed with Acid)	15	217.3045	33.8505	46.7761	93.7659	
Nickel D 5863 (mg/kg) Method A AAS (Decomposed with Acid)	14	52.4349	7.6381	9.3711	21.1575	

Analyte	No. Valid Results	Robust[a] Mean	Robust[a] Standard Deviation	Reproducibility ASTM Standard	Reproducibility These Test Data	Comments
Iron D 5863 (mg/kg) Method A: AAS (Decomposed with Acid)	12	22.9000	11.7545	See Comments	32.5600	The ASTM precision statement addresses the concentration range of iron from 3 mg/kg to 10 mg/kg. The Robust Mean is above this range, therefore ASTM Reproducibility not determined.
Vanadium D 5863 (mg/kg) Method B: AAS (Sample Diluted with an Organic Solvent)	11	232.2333	16.4895	158.7067	45.6759	
Nickel D 5863 (mg/kg) Method B: AAS (Sample Diluted with an Organic Solvent)	9	55.9429	6.8828	4.2764	19.0654	
Sodium D 5863 (mg/kg) Method B: AAS (Sample Diluted with an Organic Solvent)	9	18.1313	12.8341	12.5106	35.5505	The Test Report Data Sheet requested labs to report Method B Iron results. Method B does not address iron. The report sheet should have requested sodium. The heading of this table has been corrected to reflect sodium. There is potential that the data may reflect a combination of iron and sodium results.
Viscosity, Kinematic D 445 (mm^2/s) 100 °C	84	31.8699	1.7367	1.5948	4.8107	Eleven labs reported that their test results were initially developed in °F.
Water and Sediment D 1796 (vol %)	81	0.073	0.038	0.110	0.105	

[a] Robust statistics are computed using all the valid data, but with unusually large or small observations having limited influence on the estimates [1].

ASTM Standards

D 93-96	Test Methods for Flash Point By Pensky-Martens Closed Cup Tester
D 97-96	Test Method for Pour Point of Petroleum Products
D 129-95	Test Method for Sulfur in Petroleum Products (General Bomb Method)
D 189-95	Test Method for Conradson Carbon Residue of Petroleum Products
D 240-92 ,1	Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter
D 287-92 (1995)	Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)
D 445-94 ,1	Test Method of Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)
D 473-81 (1995) ,1	Practice for Sediment in Crude Oils and Fuel Oils by the Extraction Method
D 482-95	Test Method for Ash From Petroleum Products
D 1298-85 (1990) ,1	Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
D 1548-92 ,1	Test Method for Vanadium in Navy Fuel Oil
D 1552-95	Test Method for Sulfur in Petroleum Products (High-Temperature Method)
D 1796-83 (1990)	Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)
D 2622-94	Test Method for Sulfur in Petroleum by X-Ray Spectrometry
D 3228-96	Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method
D 3279-90	Test Method for n-Heptane Insolubles
D 4294-90 (1995) ,1	Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy
D 4629-96	Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection
D 4870-94	Test Method for Determination of Total Sediment in Residual Fuels by Spot Test
D 5291-96	Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants
D 5453-93	Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence
D 5708-95a	Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry
D 5762-95	Test Method for Nitrogen in Petroleum and Petroleum Products by Boat/Inlet Chemiluminescence
D 5863-95	Test Method for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption

,1 Indicates that only editorial changes were made to the previous issuance of the ASTM standard.

REFERENCE

[1] *Robust Statistics – How Not to Reject Outliers*; by the Analytical Methods Committee of the Royal Society of Chemistry, *Analyst*, Vol. 114, pp. 1693-1697 (1989).